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## Porewater chemistry in claystones in the context of radioactive waste disposal

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### Abstract

The development of a combined experimental-modelling approach has enabled to constrain the porewater chemistry of different low-permeability clay formations (Boom Clay, Callovo-Oxfordian Fm., Opalinus Clay) foreseen as host rocks for nuclear waste repositories. A variety of methods are available to directly sample porewater or to derive information on the solute concentrations. These include analysis from seepage waters in boreholes, aqueous extractions, high-pressure squeezing, and advective displacement from core samples. Geochemical equilibrium modelling is used for data integration and calculation of internally consistent reference water compositions. The paper provides an overview of current achievements in experimental developments, modelling approaches and open questions.

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### 1. Introduction

Deep-seated low-permeability claystones are foreseen as host rocks for nuclear waste repositories in a number of countries. The 'pristine' porewater in the far field of the repository defines the radionuclide speciation and therefore is important regarding their mobility<sup>1</sup>. In addition, it is an important basis for evaluating the impact of the repository on the host rock (e.g. oxidizing condition during early stages) and for assessing the long term behavior of the

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technical barriers (cement, bentonite backfill, canister). The nanoporous structure of claystones makes it difficult to sample and analyze the porewater solutes without inducing artefacts<sup>2,3</sup>. Generally, a multi-method approach including modelling has to be applied to constrain the porewater chemistry. At a recent international workshop, the status of knowledge of porewater chemistry in three different hostrocks – the Boom Clay (B), the Callovo-Oxfordian formation (F) and the Opalinus Clay (CH) – was discussed<sup>4</sup>. Here we present the state of knowledge of porewater chemistry by evaluating experimental and modelling aspects and their limitations and pertaining uncertainties.

## 2. Evaluation of experimental methods

### 2.1. Seepage waters from underground research laboratories (URLs)

Extraction of waters seeping into packed-off boreholes induced by a large pressure gradient is a common direct sampling method. Various disturbances may be caused e.g. by air drilling leading to oxidation of sulfides and alteration of the solute chemistry around the borehole<sup>2,4,5</sup>. Improvements of the experimental setup, including drilling with N<sub>2</sub>, have helped to reduce artefacts and enabled fairly reliable water and gas analyses. Nevertheless, microbial activity during the extended sampling periods may affect the sulfur, iron and carbonate systems.

### 2.2. Aqueous extracts, core squeezing, advective displacement

With proper handling (i.e. fast conditioning to avoid water and gas loss and oxidation) of the drill cores and anoxically conducted sample preparation, valuable data from aqueous extraction tests can be obtained. Such extraction delivers total inventories of free components not affected by mineral-water reactions (e.g. Cl<sup>-</sup>, Br<sup>-</sup>). This enables the determination of in-situ anion concentrations if water content, density and the anion-accessible porosity (see below) are known<sup>2</sup>.

The porewater concentrations of reactive species cannot be directly obtained from aqueous extracts because these are affected by fast ion exchange processes at clay-mineral surfaces (cations, section 2.3) and possibly by mineral reactions (cations, anions). Sulfate, for instance, is considered as free component in Boom Clay<sup>5</sup>, whereas it is thought to be controlled by celestite solubility in the Callovo-Oxfordian Fm (COx)<sup>6</sup> and possibly also in the Opalinus Clay (OPA)<sup>7,8</sup>.

High-pressure squeezing of well-preserved cores has been used to sample porewater of the three clay formations. A broad range of constituents can be analyzed in these waters, but special care must be taken to the interpretation of the carbonate system and all redox species. The effect of anion exclusion, arising from the repulsion of anions from the negatively charged clay surface, can be estimated from the solution obtained at the lowest pressure and the total Cl and water inventories<sup>9,10</sup>. The anion-accessible porosity has been estimated to be about 50% of the total porosity for OPA and its argillaceous confining units for clay-mineral contents above ~25 wt%<sup>8,10</sup> (Fig. 1). Stepwise squeezing suggests that there is a formation-specific threshold pressure above which disturbing effects, such as shift in electrostatic equilibrium during the squeezing process, ion filtration and pressure-dissolution of carbonates, affect solute chemistry<sup>9,10</sup>. Threshold pressures depend on mineralogy and pore-space architecture and have been reported to be in the range of 150–200 MPa for the overconsolidated COx and OPA<sup>2,4,9</sup> but are considerably lower (~20 MPa) for the plastic Boom Clay<sup>4</sup>. Porewater sampling by advective displacement was developed and applied<sup>7,11</sup> in order to obtain a few early displaced samples having very small volumes with as little as possible disturbance. Important prerequisites are well-preserved drill core samples, careful handling, and analytical methods geared towards characterizing small porewater samples. Benefits are characterization of both cations and reactive anions (sulfate), and, analogous to squeezing, determination of anion-accessible porosity when comparing leached concentrations of chloride with extracted ones.

### 2.3. Cation exchange methods and pCO<sub>2</sub> measurements

The cation exchange capacity (CEC) and exchangeable cation population are important parameters to constrain porewater chemistry. They are often determined by the Co-hexamine or Ni-ethylenediamine techniques, which have yielded fairly reliable data<sup>2,6,7</sup>. Systematic differences between these two methods have, however, been noted and

have not yet been entirely resolved. So far mineral dissolution, redox reactions during extraction and dependencies on solid/liquid ratio and extraction time have been identified as possible perturbing effects.

The partial pressure of  $\text{CO}_2$  ( $p\text{CO}_2$ ) is linked to pH via the carbonate system in carbonate-bearing clay formations. In addition to data from seepage waters or advective displacement, the  $p\text{CO}_2$  has been estimated through measurements of degassed  $\text{CO}_2$  from drill cores in specifically-designed cells under an inert gas atmosphere<sup>12</sup>. The near-to-constant value of  $p\text{CO}_2$  reached after several months in the gas-phase of the cells is used as a proxy for in-situ  $p\text{CO}_2$ . The obtained values are in agreement with in-situ measurements in COx<sup>11</sup> and OPA<sup>8</sup>, but uncertainties with regard to extrapolation of the proxy  $p\text{CO}_2$  data to the “true”  $p\text{CO}_2$  remain.

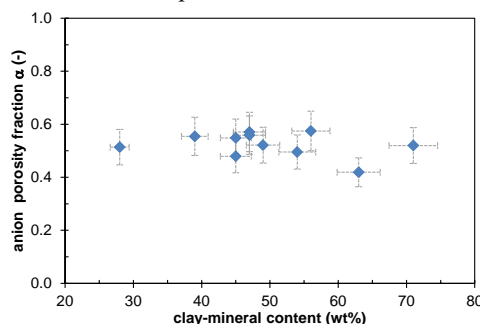


Fig. 1. Anion-accessible porosity fraction ( $\alpha$ ) derived from chloride data of samples squeezed at 200 MPa (from deep borehole SLA-1, Schlattingen, NE-Switzerland) as function of clay-mineral content in Opalinus Clay and confining units.

### 3. Advances in modelling

#### 3.1. Chemical equilibrium models

The chemistry of major solutes can be adequately described by equilibrium modelling accounting for anion exclusion via a fixed anion-accessible porosity fraction. In the “classical” model<sup>2</sup>, cation exchange and carbonate mineral (calcite and sometimes dolomite) equilibria are considered. In this type of model, the carbonate system is underconstrained according to the Gibbs phase rule and  $p\text{CO}_2$  needs to be fixed<sup>2,4,8,13,14</sup>. This parameter may be estimated from  $p\text{CO}_2$  measurements<sup>2,8</sup>, although these are inflicted with uncertainty (see above).

An alternative model considers selected phyllosilicate equilibria in addition to carbonate minerals and cation exchange<sup>6,14</sup>. In this way, the system is entirely constrained, i.e.,  $p\text{CO}_2$  is not an input parameter. In this approach, the expert opinion regarding  $p\text{CO}_2$  is replaced by the expert choice of clay mineral phases with which the pore water is in equilibrium. However, this approach is similarly disputable in view of the uncertainties related to composition and thermodynamics of clay phases. Notwithstanding such conceptual issues, similar results in terms of  $p\text{CO}_2$  as with other methods could be obtained by including clay mineral equilibria in the model<sup>6,14</sup>.

#### 3.2. Multicomponent diffusion models

The exclusion of anions induces a lower diffusive flux and a lower diffusivity of these species compared to water tracers (e.g. tritium). Cations on the other hand display higher effective diffusivities than water tracers under steady-state conditions, which may be explained by surface diffusion effects. These phenomena have been integrated in a double porosity multicomponent diffusion (MCD) model which considers ionic strength dependent diffusion in the electrostatic double layer and in the “free” solution<sup>15</sup>. Support for this model approach is provided by a recent in-situ experiment (termed DR-A) at the Mont Terri URL in OPA, in which the effect of a high salinity solution on the diffusion of  $\text{Cs}^+$  and of major constituents was studied<sup>4</sup>.

### 4. Pertaining uncertainties

We would like to highlight the following open questions with regard to porewater chemistry in claystones:

- *pH/pCO<sub>2</sub>*: Although the pCO<sub>2</sub> conditions in the claystone porewaters can be constrained within acceptable uncertainty limits, there remains ambiguity with regard to the pH-pCO<sub>2</sub> relationship and the pH buffering processes in these lithologies. This topic is linked to the uncertain role of silicate minerals in equilibrium modelling.
- *Organic carbon in chemical equilibrium models*: Currently, the models do not consider dissolved or particulate organic species, which is primarily due to the complexity of organic matter in these rocks and to the general lack of knowledge in this regard. Whilst the dissolved organic carbon (DOC) levels in COx and OPA are thought to be fairly low (a few mg C/L)<sup>4</sup>, these are fairly high in Boom Clay (>100 mg C/L)<sup>4</sup>. In fact, recent work on Boom Clay indicates strong coupling between porewater chemistry and organic matter<sup>4</sup>.
- *Redox conditions*: From the mineralogical assemblage the conditions are considered to be reducing and commonly SO<sub>4</sub>/pyrite equilibrium is assumed to control the redox potential in the three claystones<sup>2,5,6</sup>. Experimental solute data supporting this assumption are scarce and partly doubtful due to the difficulty in maintaining a reducing environment.
- *Trace metals*: The concentrations of dissolved trace metals (e.g. Ni, Zn, Co) and their solubility controls are not well constrained by available data. This, however, may be important to evaluate sorption competition by diffusing radionuclides.

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